As-Deposited Thin-Film Battery Cathode Layers

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At present, the best thin film battery cathode layers require either an elevated temperature growth environment[1] or a high-temperature (~700 °C) post-deposition anneal step to encourage the formation of the crystalline microstructure that is associated with dramatically increased battery capacity.[2] These steps are not necessarily compatible with SOI back-end processing methodology, posing a problem for any application that calls for the direct integration of the battery into a micro-circuit. The goal of this work is to create, via the manipulation of growth parameters and sputter target composition, Li-based cathode layers grown at room temperature that perform relatively well in a thin film battery setting *as deposited.*

To this end, a systematic study of rf magnetron sputtered $LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ films has been undertaken in an attempt to relate growth conditions to film composition, microstructure, and electrochemical performance. Films were grown to a thickness of ~0.3 µm in sputter gases (pressures from 2 to 20 mTorr) consisting of Ar and O_2 mixed at various ratios. Typical cathode forward power was 100 W, while the substrates could be biased using a DC or an rf power source. Film structure and texturing was subsequently examined using x-ray diffraction and TEM, while composition was determined using a combination RBS, ICP-MS, EELS, and PIGE. The electrochemical performance of the layers (both in liquid electrolyte 1/2 cells and thin-film batteries) was studied using cyclic voltometry, and impedance spectroscopy.

Results show that both target composition and substrate bias can dramatically affect film microstructure and performance. For example, figure 1 shows cycling results from liquid electrolyte 1/2 cells made from films sputtered from $LiCoO_2$ targets in a 9/1 Ar/O_2 gas mix with and without rf substrate bias. The film grown with bias has a significantly higher capacity than the film grown with no bias. This effect has been related to both film composition and microstructure.

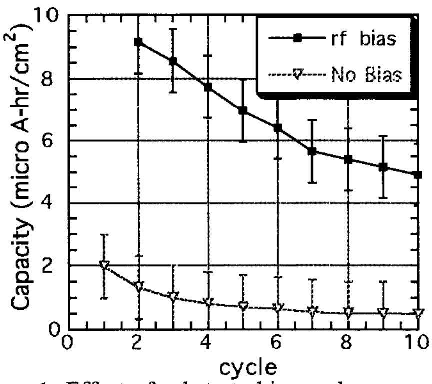

Figure 1: Effect of substrate bias on layer capacity.

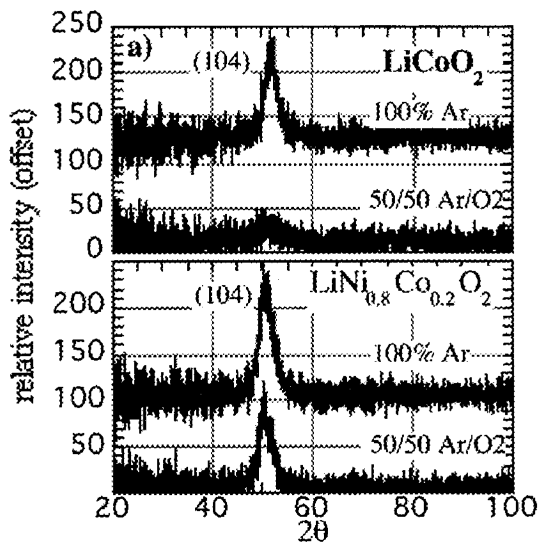

Figure 2: XRD patterns of cathode layers.

Another relevant finding concerns the X-ray data (figure 2) collected from $LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ films deposited in pure Ar and a 50/50 Ar/O_2 mix.

The diffraction patterns indicate that, contrary to results published elsewhere[3,4], it is possible to grow crystalline (grain size ~ 10nm) $LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ films with a strong (104) out of plane texture.

The texturing in the $LiCoO_2$ film is strongly dependent upon the O_2 content of the sputter gas, whereas the $LiNi_{0.8}Co_{0.2}O_2$ films maintained much of their texture despite the presence of O_2.

These findings are relevant since increased cathode capacity has been found to be related to both the degree of (104) out of plane texture[5] as well as sputter gas O_2 content.[6]

All findings will be discussed in the context of previous theoretical and experimental findings that address the structure-composition-performance relationship for thin-film solid state electrodes.

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[1] N.J. Dudney et al., J. Electrochem. Soc. **146**(7) 2455-2464 (1999)
[2] Bates et al. J. Power Sources **54**, 58-62 (1995)
[3] H. Benqlilou-Moudden et al., Thin Solid Films, **333**, 16-19 (1998).
[4] P. Fragnaud et al., J. Power Sources 63 187-191 (1996)
[5] F.X. Hart et al., J. Appl. Phys, **83**(12) 7560 (1998)
[6] W.C. West et al, Fall 1999 ECS proc. (in press)